Seasonal and stormflow dynamics of Dissolved Organic Carbon in a Mediterranean mountain catchment (Vallcebre, Eastern Pyrenees)

Running title: Seasonal and stormflow dynamics of Dissolved Organic Carbon

Maria Roig-Planasdemunt[1], Pilar Llorens[1], Jérôme Latron[1]

[1] *Institute of Environmental Assessment and Water Research (IDAEA), CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain*

Maria Roig-Planasdemunt
Institute of Environmental Assessment and Water Research (IDAEA), CSIC
Jordi Girona 18-26, 08034 Barcelona, Spain
maria.roig@idaea.csic.es
+34 934006100 ext:1621

Pilar Llorens
Institute of Environmental Assessment and Water Research (IDAEA), CSIC
Jordi Girona 18-26, 08034 Barcelona, Spain
pilar.llorens@idaea.csic.es
+34 934006100 ext:1620

Correspondance to:

Jérôme Latron
Institute of Environmental Assessment and Water Research (IDAEA), CSIC
Jordi Girona 18-26, 08034 Barcelona, Spain
jerome.latron@idaea.csic.es
+34 934006100 ext:1671

This work was supported by the Spanish Ministry of Economy and Competitiveness under Grants RespHiMed (CGL2010-18374) and EcoHyMed (CGL2013-43418). M. Roig-Planasdemunt was beneficiary of a pre-doctoral FPI grant (BES-2011-045862) and Jérôme Latron was beneficiary of a 'Ramon y Cajal' contract.

Abstract

To improve understanding of DOC dynamics in seasonal Mediterranean environments, rainfall, soil water, groundwater and stream water samples were taken during a 27-month period in the Can Vila catchment (NE Spain). Using these data, we characterised DOC dynamics in the different hydrological compartments and analysed the factors affecting them. We also analysed DOC dynamics during storm events and the factors that control DOC delivery to the stream. Results show some seasonality in rainwater and soil water DOC concentrations, while no clear seasonality was observed in stream water and groundwater, where DOC dynamics were strongly related to discharge and water table variations. For storm events with several discharge peaks, the slope of the discharge/DOC concentration relationship was higher for the first peak. The rather similar dynamics of stream water DOC concentration in all floods contrast with the observed diversity of hydrological processes. This raises the question of the origin of the observed rapid DOC increase.

Keywords: Dissolved Organic Carbon (DOC), Seasonal dynamics, Stormflow dynamics, Runoff processes, Mediterranean area, Vallcebre Research Catchments

1. INTRODUCTION

In hydrological studies, Dissolved Organic Carbon (DOC) is increasingly considered an important stream water constituent of organic origin. DOC is scavenged by precipitation, enriched during throughfall and leached from organic matter, contained in soils or stored in the channel bed (Meyer and Tate 1983, Baron *et al.* 1991). When travelling through a catchment, DOC is often affected by hydrological and biochemical processes operating within the catchment. For this reason, the study of DOC dynamics in different pools and at different time scales has been used in the last three decades to characterise water origin and flow components, with the objective of improving our understanding of catchment hydrological functioning (Mulholland and Hill 1997, Kendall *et al.* 1999, McGlynn and McDonnell 2003, Morel *et al.* 2009).

On the annual scale, DOC concentration in rainwater may show some seasonality (Pan *et al.* 2010, Verstraeten *et al.* 2014). However, rainfall or throughfall are not the main sources of DOC in soil solution (Verstraeten *et al.* 2014); and seasonality observed in soil water DOC concentration is indeed associated with the time sequence of different processes, both biochemical and hydrological ones, acting in soils. Higher concentrations are observed during the growing season, while lower concentrations follow DOC losses due to water fluxes during the wet period (Meyer and Tate 1983, McDowell and Wood 1984, Buckingham *et al.* 2008, Verstraeten *et al.* 2014). The decrease in DOC concentration with depth in the soil profile, as organic matter content decreases, implies low DOC concentration in groundwater (Boyer *et al.* 1997, Aubert *et al.* 2013). Besides, no clear seasonality is observed in deep soil water and groundwater DOC concentrations (Neal *et al.* 2005, Clark et al. 2008). Finally, even though DOC concentration in stream water has been studied mainly during storm events, several studies also showed some seasonality of stream water DOC concentration during the year (Eshleman and Hemond 1985, Evansa *et al.* 1996, Bernal *et al.* 2002, Neal *et al.* 2005, Dawson *et al.* 2011).

On the storm event scale, the vast majority of studies, in catchments under different climates, reported an increase in stream water DOC concentration with increasing discharge during rainstorm or snowmelt events. This general behaviour leads to a positive correlation between stream water DOC concentration and discharge and implies that the main export of DOC occurs during storm events (Meyer and Tate, 1983, Soulsby, 1995, Hinton *et al.* 1997, Butturini and Sabater 2000, Carey 2003, Neal *et al.* 2005, Stutter et al. 2012).

DOC concentration's increase with increasing discharge is generally explained by DOC being flushed from the shallow soil horizons by rising water tables or by infiltrating rainfall (Meyer and Tate 1983, McDowell and Likens 1988, Hinton *et al.* 1998). McGlynn and McDonnell (2003) pointed out that in upland catchments, prior soil moisture conditions and the degree of connection between runoff contributing areas and the stream may influence this increase in DOC concentration observed at the catchment outlet. The correlation between DOC concentration and discharge has therefore led some authors to use DOC as a tracer to identify the contribution of water from organic soil layers during storm events (Ladouche et al. 2001, Carey and Quinton 2005, Morel et al. 2009). However, the flushing of organic matter stored in the streambed has also been identified as an alternative source of DOC in stream water (Mulholland and Hill 1997, Meyer *et al.* 1998, Bernal *et al.* 2002), somehow questioning the use of DOC as a usefull tracer of water origin.

During the last 30 years, most studies of stream water DOC dynamics, both during storm events and throughout the year, have been carried out in humid (Hinton *et al.* 1997, Inamdar *et al.* 2004, Neal *et al.* 2005, Morel *et al.* 2009, Dawson *et al.* 2011), alpine (Baron *et al.* 1991, Boyer *et al.* 1997) and polar regions (Peterson *et al.* 1986, Ivarsson and Jansson 1994, Hudon *et al.* 1996, Carey, 2003). However, as Llorens *et al.* (2011) comment, Mediterranean catchments have received less attention.

Regions with Mediterranean climate are characterised by strong intra- and inter-annual precipitation variability and a marked seasonality of the evaporative demand, which define the seasonality of this climate, characterized by a drier period during the year. In consequence, Mediterranean catchments often share hydrological processes of both wet and dry environments (Gallart *et al.* 2002), which makes it harder to understand their hydrological and biogeochemical behaviour through the year (Latron *et al.* 2009, 2010a, Llorens *et al.* 2011).

DOC concentrations in Mediterranean pristine catchments and export from them fall into the low range of those measured worldwide (Alvarez-Cobelas *et al.* 2012). For example, Von Schiller *et al.* (2008) reported mean stream DOC concentrations of 1±0.37 mgl^{-1} in 5 pristine catchments, located in NE Spain. Different DOC dynamics have however been observed in some Mediterranean catchments located very close to one another. The increase in stream water DOC concentration with increasing discharge described in the La Riera Major catchment (Butturini and Sabater 2000) was less clear in the nearby Fuirosos catchment except for large events, suggesting for this catchment a change in the water pathways under wet conditions (Bernal *et al.* 2002). However, for both these catchments a clear increase in stream DOC concentration during the wetting-up period was reported, due to the leaching of organic matter accumulated on the streambed and the stream bank during the drought period (Butturini and Sabater, 2000, Bernal *et al.* 2002, Vázquez *et al.* 2007). This process, more specific of seasonal streams, probably contributes to increasing the diversity of DOC-discharge responses observed during storm events in Mediterranean catchments (Butturini *et al.* 2008).

This study, performed in the Can Vila research catchment (NE Spain), focused on the analysis of DOC concentration dynamics in different water compartments (rainfall, soil water, groundwater and stream water) through the year and during storm events. The specific objectives are (i) to characterise DOC dynamics in rainfall, soil water, groundwater and stream water during the year and (ii) to analyse DOC dynamics during storm events to assess possible differences in the hydrological functioning of the catchment during the year (iii) to discuss the validity of the use of DOC as tracer to identify water sources during rainfall events in Mediterranean catchments.

2. METHODS

2.1. Study site

This study was performed in the Can Vila research catchment, located in the Vallcebre research area (Latron *et al.* 2010a) at the headwaters of the Llobregat River, on the southern margin of the Pyrenees, NE Spain (42°12' N, 1°49' E). The Vallcebre research area, managed by the Surface Hydrology and Erosion group (IDAEA-CSIC), was selected in early 1990 to analyse the hydrological consequences of land abandonment and the hydrological and sediment yield behaviour of badlands areas. A complete overview of the general hydrological findings can be found in Latron *et al.* (2009, 2010a, 2010b), Llorens *et al.* (2010) and Gallart *et al.* (2010).

The Can Vila catchment (Fig. 1) has an area of 0.56 km^2. Elevations range from 1,458 m a.s.l. to 1,115 m a.s.l. at the outlet and slope gradients are moderate, with a mean value of 25.6% (Latron and Gallart, 2007). The soils that have developed over red clayey smectite-rich mudrocks are predominantly of silt-loam texture. Topsoils are rich in organic matter (on average 4.1% from 0 to 55 cm below the ground surface) and well structured, with high infiltration capacity, although hydraulic conductivity decreases rapidly with depth (Rubio *et al.* 2008). Before and during the 19th century most of the hill-slopes of the catchment were deforested and terraced for agricultural purposes. They were abandoned during the second half of the 20th century. As a consequence of terracing, soil thickness ranges from less than 50 cm in the inner part of the terraces to more than 2 or 3 m in their outer part (Latron *et al.* 2008). Following land abandonment, spontaneous forestation by *Pinus sylvestris* has occurred (Poyatos *et al.* 2003) and forest now covers 34% of the catchment. The remainder of the catchment is widely covered by pasture and meadows. The main channel is a first order channel of 1 to 2 m wide and is not very deeply incised. The stream bed is a riffle-pool sequence, the materials being mostly formed by coarse alluvium partly cemented by lime coatings. Mobile sediments are mostly fine sands and silt. No riparian zone is observed in the catchment.

Climate is humid Mediterranean, with a marked water deficit in summer. The mean annual rainfall is 862 ± 206 mm, with a mean of 90 rainy days per year (Latron *et al.* 2009). Snowfalls account for less than 5% in volume. The rainiest seasons are autumn and spring. Winter is the season with the least precipitation. In summer, convective storms may provide significant precipitation input. Mean annual temperature at 1,260 m a.s.l. is 9.1ºC and mean annual potential evapotranspiration is 823 ± 26 mm (Latron *et al.* 2010a).

The combined dynamic of rainfall and evapotranspiration favours the succession of wet and dry or very dry periods during the year (Latron and Gallart, 2007, 2008). Dry and very dry periods occur in winter and summer, respectively, whereas wet periods correspond to spring and late autumn. Over the period 1995-2013, mean annual runoff in the Can Vila catchment was 302 ± 191 mm, representing 34% of rainfall (Latron *et al.* in prep.). Streamflow shows marked seasonality and often dries in summer for several weeks.

2.2. Hydrometric monitoring

Rainfall in the Can Vila catchment is recorded every 5 min by means of three 0.2 mm tipping-bucket rain gauges (Casella Cel), located 1 m above the ground (Fig. 1). A standard meteorological station is located in the upper part of the catchment.

At the Can Vila gauging station, streamflow is measured by means of a 90º V-notch weir with a water pressure sensor (6542C-C, Unidata) connected to a datalogger (DT50, Datataker). Mean water level values (measured every 10 seconds) are recorded every 5 min and converted to discharge values with an established stage-discharge rating curve calibrated with manual discharge measurements (Latron and Gallart 2008).

Water table data used in this study were collected in two piezometers, Z_{CV08} (-4220 mm deep) and Z_{CV35} (-2062 mm deep) (Fig. 1). The water table level was recorded every 10 min by means of a water pressure sensor (10m MiniDiver, Schlumberger Water Services), adjusted with barometric pressure variations. Pressure sensors were calibrated by taking manual measurements of water table depth at the piezometers at the same time as data collection.

Soil water content data used in this study were obtained from a set of 3 automatic 30 cm long time-domain reflectometry (TDR) probes (CS616,Campbell), inserted vertically from 0 to 900 mm depth (Fig. 1). TDR probes were connected to a datalogger (DT500, Datataker) that recorded mean frequency values every 5 min. Frequencies were subsequently converted to soil water content values, using, for each probe, linear regression between frequency and soil water content obtained from weekly manual TDR measurements (Tektronix 1502-C cable tester) at the same depth intervals.

Soil temperature was measured (Termistor 107, Campbell) every 5 min at 200 mm depth close to the TDR profile.

2.3. DOC water sampling and laboratory analyses

Rainwater was sampled automatically, at 5mm rainfall intervals, using an open collector (34 cm diameter) connected to an automatic water sampler (24*500 ml bottles, ISCO 2900). The rainfall sampling site is located at the outlet of the catchment (Fig. 1). To eliminate the effect of the possible washing of the open collector at the beginning of rainfall, the first sample of rainfall events was discarded. The last rainfall sample was also excluded when less than 1mm was collected.

Stream water was sampled at the gauging station with two automatic water samplers (24*1000ml bottles, ISCO 2700). Both samplers were triggered by the datalogger (DT50, Datataker). One sampler took samples at variable time intervals (depending on water level changes), once a predetermined water level threshold, defining flood conditions, was reached. The other sampler took a daily sample at 00h00. Water samples were collected just after a rainfall/runoff event. In the absence of flood, only a weekly sample from the automatic sampler was kept.

In addition to rainfall-runoff automatic sampling, spatially distributed water samples were taken every two weeks, in order to characterise the seasonality of DOC sources. Soil water was sampled at two locations in the catchment (L_{CV01} and L_{CV02}, see Fig. 1), with a battery of suction cup lysimeters installed between 500 and 900 mm depth. The soil water sample at each location was a mix of the water collected at different depths. Groundwater was sampled at locations Z_{CV08} (4220 mm deep) and Z_{CV35} (2080 mm), at maximum piezometers depth, using a manual peristaltic pump. Finally, stream water was sampled manually (grab sample) at the gauging station.

During the study period, 958 samples were collected and analysed. This total corresponds to 187 rainwater, 92 soil water, 102 groundwater and 577 stream water samples. Of the stream water samples, 228 corresponded to flood conditions.

All samples were collected in 120 ml opaque muffled glass bottles and filtered in the laboratory through a 0.45µm membrane filter (Millipore). Subsamples were then acidified with HCl (2 N) and stored at 4ºC in cleaned and muffled glass bottles. DOC analyses were performed within one week.

The DOC concentration value was the average of 3 measurements for each sample, using a Total Organic Carbon Analyzer (TOC-VCSH/CSN, Shimadzu). The detection limit measured was 0.06 mg l^{-1}, following the method of Rubinson and Rubinson (2000).

2.4. Data analyses

The study reported here, investigating both seasonal and event scale dynamics, is based on hydrometric and DOC data covering a 27-month period from May 2011 to July 2013. During this period, 11 significant rainfall-runoff events (i.e. with a peak discharge higher than 20.0 l s^{-1} km^{-2}) were recorded and sampled. At the event scale, storm runoff depth was derived for each selected significant rainfall-runoff event, using the classic "constant slope" hydrograph separation method of Hewlett and Hibbert (1967) with a modified slope value of 1.83 l s^{-1} km^{-2} d^{-1} (see Latron *et al.*, 2008). For each rainfall-runoff event, several variables were finally derived from the hyetograph and hydrograph. These were rainfall depth, storm runoff coefficient, pre-event (at the start of the event) and peak flow specific discharges. At the event scale, the slope of the linear relationship between stream water DOC concentrations and specific discharges (at the time the samples were taken) was also determined. Soil water content, water table depth and stream water DOC concentration at the start and at the peak of the event were identified (Table 2).

As DOC concentrations and dynamics throughout the year are likely to be influenced by temperature, biological activity and the hydrological conditions of the catchment, the data of the whole study period were grouped in 4 different periods, as in Bernal *et al.* (2005). These 4 periods were: dormant period (December to March), vegetative period (April to July), dry period (August) and wetting-up period (September to November). The correlation between variables was assessed by the Pearson correlation coefficient. The correlation was considered statistically significant if $p < 0.05$.

3. RESULTS

3.1. DOC dynamics throughout the year

3.1.1. DOC dynamics in rainfall, soil water, groundwater and stream water

During the 27-month study period (May 2011 to July 2013), 41 rainfall events were sampled at 5mm rainfall intervals. Events sampled ranged from 5.6 to 74.8 mm (median value = 24.2 mm), most of which occurred during the vegetative period (23 events). 11 rainfall events were sampled during the wetting-up period and 7 during the dormant one. All events taken together gave a mean (± standard error) DOC concentration in rainwater of 1.1 ± 0.06 mg l^{-1}. DOC concentration in rainwater followed a seasonal dynamic each year (Fig. 2), with higher DOC concentrations during the vegetative period (1.3 ± 0.08 mg.l^{-1}). During the dormant period, the average DOC concentration was 0.5 mg l^{-1} lower than the mean value of the vegetative period (Table 1). The variability of DOC in rainwater during rainfall events was similar in all periods, with an average standard error of the mean close to 0.1 mg.l^{-1}. Taking into account all rainfall events, no relationship between the mean DOC concentration in rainwater and rainfall depth or intensity (in 30 minutes) was found. The same result was obtained after grouping the rainfall events in periods.

From May 2011 to July 2013, mean DOC concentration in soil water was 6.5 ± 0.31 mg l^{-1} at L_{CV01} and 16.7 ± 1.42 mg l^{-1} at L_{CV02}. Despite the difference in the absolute values between the two sites, significant linear regression (r^2=0.53, p<0.01) and a similar temporal evolution of soil water DOC concentration at both locations were observed. The seasonal dynamics of soil water DOC concentrations at L_{CV01} are shown in Fig. 3(b). They followed a sinusoidal trend (r^2=0.39, p <0.01), with higher DOC concentrations during the vegetative, dry and wetting-up periods and lower ones during the dormant one (Table 1). This dynamic was similar to the soil temperature dynamic and inverse to the dynamic observed in soil water content. Thus, higher DOC concentrations occurred under dry soil conditions, when soil temperature was high (Fig. 3(a)). At $L_{CV01,}$ soil water DOC concentration correlated positively with soil temperature (r^2=0.36, p<0.01) and correlated negatively, though slightly, with soil water content (r^2=0.16, p <0.01). These relationships were not so clearly observable at L_{CV02}, partly because of the fewer samples collected.

Mean DOC concentration in groundwater was 2.9 ± 0.19 mg l^{-1} at Z_{CV08} and 5.6 ± 0.4 mg l^{-1} at Z_{CV35}. DOC concentration absolute values and dynamics were different between the two sites. No clear seasonal dynamic of DOC concentration was observed (Table 1) and some of the lowest values of DOC concentrations were observed in all periods. At Z_{CV08} (but not at Z_{CV35}), groundwater DOC concentrations were strongly related to the dynamics of the water table and both variables correlated positively (r^2=0.37, p<0.01), with an increase in DOC concentrations when the water table level rises (Fig. 3(c)). DOC concentrations down to 1.0 mg l^{-1} were measured when the water table was at its lowest (-3500mm), whereas they reached 6 or 7 mg l^{-1} when the water table was close to the surface.

Mean DOC concentration in stream water during the study period was 2.7 ± 0.05 mg l^{-1} at the catchment outlet. Considering only low flow conditions (specific discharge lower than 20 l s^{-1} km^{-2}), mean DOC concentration in stream water was 2.1 ± 0.03 mgl^{-1}; whereas for flood conditions (discharge higher than 20 l s^{-1} km^{-2}), it was 3.5 ± 0.09 mgl^{-1}. DOC concentration in stream water increased markedly during storms, up to values of 6 to 10 mg l-^{1} for larger flood peaks. Consequently, there was no apparent seasonality in stream water DOC concentration (Table 1). Changes in DOC concentrations appeared to be more influenced by stream discharge dynamics than by biological activity (Fig. 3(d). For low flow conditions, DOC concentrations showed few variations and there was no seasonality in DOC concentration here, either. While there was a positive significant correlation between DOC concentration and discharge during flood conditions (r^2=0.47, p<0.01, Fig. 4), for low flows a weak positive correlation was observed (r^2=0.08, p<0.01).

3.1.2 Relationship between DOC concentrations in soil water, groundwater and stream water

As indicated above, there was a statistically significant linear relationship between soil water DOC concentrations measured fortnightly at the two sampling sites. However, no significant linear relationship existed between DOC concentrations measured at the piezometers, Z_{CV08} and Z_{CV35}.

On comparing the different water compartments at all sampling sites (using samples taken fortnightly), no significant linear relationships between soil water DOC concentrations and groundwater or stream water concentrations were found. On the contrary, a positive and statistically significant linear relationship between DOC concentration in groundwater and in stream water was found. This relationship was somewhat stronger for piezometer Z_{CV08} (r^2=0.42, p <0.01, Fig. 5a) than for Z_{cv35} (r^2=0.13, p <0.01). The relationship between the depth to the water table (Z_{CV08}) and the specific discharge (outlet of the catchment) at the time the samples were taken followed a semi-logarithmic trend (Fig. 5b),

3.2. DOC dynamics in the stream during rainfall-runoff events.

Over the study period, all 11 rainfall-runoff events with peak discharge higher than l s^{-1} km^{-2} were sampled (Fig. 3(d)). The sampled events (Table 2) cover a wide range of magnitude, with peak discharges ranging from 46.5 to more than 2400 l s^{-1} km^{-2} and runoff coefficients between 7.5 and 53.5%. Sampled events also covered a range of prior wetness conditions; with some occurring in dry conditions (19/01/2013) and some occurring in wet or very wet conditions (29/05/2012). 3 floods occurred in the dormant period, 6 in the vegetative period and 2 in the wetting-up period.

Taking all floods together, a significant positive correlation existed between the increase in DOC concentration during the flood and the increase in discharge (r^2=0.49, p <0.05). However, when taking the three larger events separately (with peak flow values 4 times higher than the rest of the floods), this correlation was no longer apparent (r^2=0.03, p >0.05). Data from the 11 floods also revealed that the magnitude of the flood correlated significantly with prior wetness conditions. Indeed, a significant positive relationship existed between the storm runoff coefficient and the soil water content (r^2=0.47, p <0.05) or the depth to the water table at the beginning of the flood (Z_{CV08} r^2=0.48, p <0.05; Z_{CV35} r^2=0.43, p <0.05). The change in stream water DOC concentrations was, however, not clearly related to prior wetness conditions and no significant linear relationship was found between the increase in DOC concentration during the flood and the soil water content (r^2=0.13 p >0.1) or the depth to the water table at the beginning of the flood (Z_{CV08} r^2=0.02, p >0.1; Z_{CV35} r^2=0.01 p >0.1). Further, significant positive correlation was found between the increase in DOC concentration during the flood and the initial (before the flood) DOC concentration in soil water at L_{CV01} (r^2=0.43, p <0.05). It was not, however, possible to confirm this finding for L_{CV02} due to the lack of data. The increase in DOC concentration during the flood was also related to the initial DOC concentration in groundwater at Z_{CV35}, even if the correlation was not significant (r^2=0.39, p >0.05). No correlation was found with initial DOC concentrations at Z_{CV08} (r^2=0.06, p >0.05).

During all floods, stream water DOC concentration followed the discharge pattern, increasing steadily during the hydrograph's rising limb, reaching the maximum concentration around peak flow and decreasing gradually during the recession (Fig. 6(a)). As a consequence of this dynamic, a mostly linear positive relationship between stream water DOC concentration and discharge existed for all events. The DOC concentration-discharge relationship showed some hysteresis (Fig. 6(b)), with higher values of DOC concentrations more frequent during the rising limb of the hydrograph than during the falling limb (i.e. positive hysteresis). Negative hysteresis was seen only during the three larger events (in terms of peak flow), characterised by an extremely rapid discharge increase (up to 650 l s^{-1} km^{-2} in 5 min).

Floods with two main discharge peaks (five events) showed that the slope of the relationship decreased from the first to the second peak (Fig. 6(b)). This indicated that, for a given value of discharge, stream water DOC concentration was always lower during the second discharge peak than during the first one. However, hysteresis observed at both peaks remained similar.

The slopes of the DOC concentration-discharge relationship for all events (and all peaks) are shown in Table 2. Excluding the three larger events (with much lower slope values most probably related to the extremely rapid discharge increase), slope values ranged from 0.001 to 0.058 (first peak) and from 0.010 to 0.020 (second peak). The slopes of the DOC concentration-discharge relationship were similar during the dormant and vegetative periods (both for the first and second peaks) and lower for the first peak during the wetting-up period (Fig. 7).

To investigate further the dynamics of DOC concentration during floods and to infer the possible causes of these dynamics, three floods that occurred in dormant, vegetative and wetting-up periods were compared (Fig. 8). The three floods were characterised by large rainfall amounts (68.8 to 98.4 mm) but by different prior wetness conditions, as shown by their different initial discharges (0.9 to 9.3 l s^{-1} km^{-2}).

The three floods presented a double peak with similar peak flow values (256 to 279 l$s^{-1}$$km^{-2}$) during the second peak. The dynamics of stream water DOC concentration during the three floods were comparable, following the discharge pattern and decreasing gradually during the recession (Fig. 8(a)). However, the DOC concentration-discharge relationship was different for the three floods during the first flood peak (Fig. 8(b)), with slopes of the relationship between 0.019 and 0.037. On the contrary, during the second peak (i.e. peak flow), the slopes of the DOC concentration-discharge relationship were much more similar (0.010 to 0.014). In all cases (first and second peaks), the DOC concentration-discharge relationship showed little positive hysteresis.

The dynamics of soil water content during the three floods showed a rapid response, regardless of the initial soil water content value. During the flood, soils were close to saturation in the vegetative and wetting-up periods, but not during the dormant period (Fig. 8(c)). The water table at Z_{CV35} showed a quick response during floods and reached temporary (wetting-up period) or permanent (dormant and vegetative periods) saturation. The water table at Z_{CV08} showed a smooth delayed response during the three floods (i.e. limited response coinciding with the first flood peak, then reaching a maximum during the second flood peak), even if its magnitude was different for the three floods (Fig. 8(c)). In consequence, saturation at Z_{CV08} was only reached for the flood in the dormant period,

whereas minimum water table depth was -283mm and -666mm for the floods in the vegetative and wetting-up periods, respectively.
The stream water DOC concentration-water table depth (Z_{CV08}) relationship showed for all floods (and all peak flows) positive hysteresis, indicating that the increase in DOC concentrations in the stream always preceded the rise of the water table at Z_{CV08} (Fig. 8(d)). No real differences were observed in this relationship between the different floods, even if the magnitude of the stream water DOC concentration increase differed between floods or in a single flood, between the first and the second peak flow. An opposite dynamic occurred in the stream water DOC concentration-soil water content relationship. For all floods (and all peak flows), negative hysteresis (i.e. soil water content increase always preceding the increase in DOC concentration in the stream) was observed (Fig. 8(e)). Again, this dynamic was common to all floods, regardless of the period considered and of the magnitude of the stream water DOC concentration increase.
Therefore, the results given in Figure 8 imply a broadly similar dynamic of stream water DOC concentration during similar floods occurring in dormant, vegetative and wetting-up periods. Only the magnitude of the stream water DOC concentration increase during the first flood peak was found to be somewhat different. These results suggest that seasonality may not play a relevant role in stream water DOC concentration dynamics during rainfall-runoff events.

4. DISCUSSION

4.1 Seasonal patterns of DOC

In the Can Vila catchment, as observed elsewhere (Meyer and Tate 1983, Hinton *et al.* 1998, Michalzik *et al.* 2001, Neal *et al.* 2005, Morel *et al.* 2009), the concentration of DOC in rainfall was lower than in soil water, groundwater or stream water (table 1). In this study, the mean annual DOC concentration in rainfall measured was 1.1 ± 0.06 mg l^{-1}, which was in the low range of mean DOC concentrations in precipitation observed in different European regions, where mean values were always lower than 2.5 mg l^{-1} (Morel *et al.* 2009, Verstraeten *et al.* 2014). Rainfall water DOC concentration showed, moreover, some seasonality, with higher values measured during the growing season (April-July) due to the increase in biological activity, as described by other authors (Pan *et al.* 2010, Verstraeten *et al.* 2014).
The low DOC concentrations normally observed in rainfall have, therefore, a limited influence on soil water DOC concentrations (Verstraeten *et al.* 2014). In the study catchment, DOC concentrations were higher in soil water than in the other water compartments, in line with results generally reported (Meyer and Tate 1983, Carey 2003, McGlynn and McDonnell 2003, Inamdar *et al.* 2004; Morel *et al.* 2009). The mean concentrations observed at the two sampling locations (6.5 ± 0.31 mg l^{-1} at L_{CV01} and 16.7 ± 1.42 mg l^{-1} at L_{CV02}) are in the order of magnitude reported in several review studies in temperate areas (Buckingham *et al.* 2008; Wu *et al.* 2010, Camino-Serrano *et al.* 2014). These reviews do not include Mediterranean areas, but as the Can Vila catchment is a humid Mediterranean mountain area 1,100m a.s.l., sharing characteristics of temperate environments during some periods of the year, it makes sense to compare Can Vila catchment DOC concentrations with those of temperate areas. Seasonal changes were observed in soil water DOC concentration. As in other studies (Meyer and Tate 1983, McDowell and Wood,1984, Buckingham *et al.* 2008, Verstraeten *et al.* 2014), the highest DOC concentrations were observed during the vegetative period till the end of wetting-up, i.e. the whole growing season (Fig. 3(b)). This DOC temporal variation reflects the succession of biochemical processes controlling DOC concentration in soils (Lambert *et al.* 2013), which are in turn affected by soil

temperature (McDowell and Wood 1984). Indeed, soil water DOC concentration and soil temperature had similar seasonal dynamics in the Can Vila catchment, with a positive statistically significant relationship between them (Fig. 3(a)). This effect of temperature on soil water DOC concentration has been described in several field and laboratory studies (Christ and David 1996, Michalzik *et al.* 2001; Wu *et al.* 2010).

The mean groundwater DOC concentrations measured in Z_{CV35} (5.6 ± 0.4 mg l^{-1}) and Z_{CV08} (2.9 ± 0.19 mg l^{-1}) were slightly higher than concentrations observed in several Mediterranean and Temperate catchments (Butturini and Sabater 2000, Neal *et al.* 2005, Vázquez *et al.* 2007, Aubert *et al.* 2013). The highest concentrations observed at Z_{CV35} may be explained by that, as it is a shallow piezometer (2080 mm deep), its DOC concentrations are similar to those usually found in soil water. At Z_{CV08} DOC concentration showed some stratification with depth, with lower concentrations, closer to the values described in the literature (Neal *et al.* 2005, Vázquez *et al.* 2007; Aubert *et al.* 2013), when the water table level was deeper than 3,500 mm, as shown in Fig. 3(c), and explained by DOC retention within mineral soil horizons by sorption (Kalbitz *et al.* 2000). Additionally, the absence of seasonal variability in groundwater DOC concentration may be explained by the low effect of temperature and of biochemical activity at this depth, as observed in other catchments (Neal *et al.* 2005).

The mean stream water DOC concentration measured at Can Vila (2.7 ± 0.05 mg l^{-1}) was comparable to the values reported in Mediterranean and Temperate catchments (Butturini and Sabater 2000, Bernal *et al.* 2002, Neal *et al.* 2005, Dawson *et al.* 2008). In the study catchment, DOC concentrations were higher during stormflow periods than during low flows, as observed in other streams (Meyer and Tate 1983, Hinton *et al.* 1997, Bernal *et al.* 2005). During storm events, DOC increased in the stream, probably due to the contribution of DOC-rich soil water, whereas during low flow periods DOC concentration in stream water was similar to the concentrations observed in groundwater (Table 1), suggesting that this was the main stream water source during low flows, especially during the dry period, as described by Schiff *et al.* (1997).

In the Can Vila catchment, as in other Mediterranean intermittent streams (Butturini and Sabater 2000), it was not possible to identify the stream water DOC seasonality usually observed in catchments with low hydrological variability (Evansa *et al.* 1996, Neal *et al.* 2005, Dawson *et al.* 2011). This was probably related to the strong variability of the hydrological regime, characteristic of Mediterranean catchments, which masks possible seasonal variations of stream water DOC concentrations. The absence of seasonality in stream water DOC concentrations may also be explained by the positive relationship observed between DOC concentrations in stream water and in groundwater (Fig. 5), where no seasonality was observed, either.

4.2 DOC dynamics in stream water during rainfall-runoff events.

During rainfall-runoff events, DOC concentration in Can Vila stream water rapidly increased with increasing discharge, leading to a positive relationship between stream water DOC concentration and discharge. This relationship is consistent with patterns observed in both humid (Meyer and Tate 1983, Hinton *et al.* 1997, Morel *et al.* 2009) and Mediterranean (Butturini and Sabater 2000) catchments. The positive relationship between DOC concentration and discharge was less apparent during base flow conditions as observed in other catchments (Singh *et al.* 2014).

The little positive hysteresis observed in this relationship (except for the largest events) is also consistent with responses described in a set of Mediterranean catchments (Butturini *et al.* 2006).

For rainfall-runoff events with several peaks, the observed decrease of the slope of the DOC concentration-discharge relationship from the first peak to the following peaks

(Fig. 6) and the rapid decrease in DOC concentration during the falling limb show that the DOC contribution was mainly flushed at the beginning of the event (during the first peak).

In the Can Vila catchment, the increase in stream water DOC concentration during floods suggests a relevant contribution of soil water (with higher DOC concentration), with storm water flowing through the upper organic soil layers, as suggested by several authors (Bishop *et al.* 2004, Laudon *et al.* 2011, McDowell and Likens 1988, McGlynn and McDonnell 2003). The rapid increase of DOC concentration in stream water in the Can Vila catchment was always followed by soil water content increase, but preceded the significant rise of the water table (Fig. 8(d) and (e)), reinforcing the idea of the relevant role of soil water. In fact, even if the absence of a distinc riparian zone in the catchment, the combination of a higher hydraulic conductivity of the upper soils (Rubio et al., 2008) and a high DOC concentration in soil water (Table 1) can explain the rapid increase of DOC concentration in streamflow as described elsewhere (Bishop *et al.* 2004, Laudon *et al.* 2011).

Moreover, the synchronism found between DOC and the discharge peak could also indicates the possibility of stream water DOC sources near or in the stream bed during rainfall events, as suggested by several authors (Hinton *et al.* 1998, Butturini and Sabater 2000, Bernal *et al.* 2002). The rapid DOC increase could correspond partly to the removal along the first flood peak of organic matter accumulated in the stream bed. In Mediterranean catchments, characterized by a succession of wet and dry periods during the year (Latron et al. 2009), several autors (Bernal *et al.* 2005, Vazquez *et al.* 2007, Von Schiller *et al.* 2015) indicated that the leaching of particulated organic matter accumulated in the streambed, specially following a dry period, can lead to a pulse of DOC in streamwater. Indeed, the accumulation of particulated organic matter in these Mediterranean streambeds was estimated being 10 times greater after a dry spell, than during a wet year, with no flow interuption (Acuña et al. 2004).

In Can Vila catchment, the DOC dynamics in response to similar discharge events seem invariant through seasons (Fig. 8). Furthermore, DOC dynamics during floods were not related to prior wetness conditions, as already shown by Bernal *et al.* (2002) in another Mediterranean catchment. The non-changing behaviour of DOC dynamics during floods contrasts with the diversity of hydrological responses in the 11 floods included in this study. As shown in Table 2, peak discharges ranged from 47 to more than 2,417 $l\ s^{-1}\ km^{-2}$ and runoff coefficients were between 7.5 and 53.5%. In addition, prior discharge, rainfall depth and rainfall intensity also differed greatly between sampled events. This changing and non-linear hydrological behaviour of the Can Vila catchment, described in Latron and Gallart (2007, 2008) and Latron *et al.* (2008), results mainly from the succession of dry and wet periods and the characteristic occurrence of wetting-up transitions between the two. The succession of these different periods increases the complexity of the rainfall–runoff relationship by triggering a different combination of hydrological processes, which depend on catchment wetness conditions.

The fact that rather similar dynamics of stream water DOC concentration were observed in all floods sampled in this study is apparently in contradiction with the observed diversity of hydrological processes and deserves further attention. In particular, the role of surface runoff (not sampled in this study), acting as a potential input of water with high DOC concentrations during some events, has to be investigated. This would help to explain whether the systematic DOC concentration increase observed during floods results from various hydrological contributions (DOC-enriched surface runoff, soil water subsurface flow, etc.). This, in turn, would confirm that different combinations of dominant hydrological processes might lead to similar DOC dynamics during a flood;

and that DOC sources and water flow paths cannot be easily inferred from catchment outflow concentrations alone, as shown by McGlynn and McDonnell (2003). For these reasons, more information is needed to use DOC as tracer to identify water sources during rainfall events in this mediterranean catchment. A better understanding of DOC sources, and especially of the DOC transfer in the soil-stream continuum (Bishop et al., 2004), combined with the hydrological process-based knowledgement of the catchment, is necessary before using DOC as an environmental tracer for runoff processes identification.

5. CONCLUSIONS

This study provides detailed information on Dissolved Organic Carbon (DOC) dynamics in a seasonal Mediterranean catchment. The data obtained on DOC concentrations in the different hydrological compartments, and at different temporal scales, give some insights into the factors that control DOC delivery to the stream.

The Can Vila catchment had some seasonality in rainwater and soil water DOC concentrations, which was related to biological activity. However, no clear seasonality was observed in stream water and groundwater, where DOC dynamics were closely related to discharge and water table variations.

During storm events, stream water DOC concentration followed the discharge pattern closely. However, in storm events with several discharge peaks a flushing of DOC during the first discharge peak and, in consequence, a reduction in DOC concentration at the following peaks were found. The increased stream water DOC concentration during floods suggests a relevant contribution of soil water, but also the existence of stream water DOC sources near or on the stream bed.

The similar stream water DOC dynamics during all the floods considered in this study clearly contrast with the diversity of their prior conditions (soil water content, rainfall characteristics…), as well as with the diversity of their magnitude (peak flow, storm-flow coefficient…). This contrast raises the question of the origin of the rapid DOC increase observed and confirms that water flow paths cannot be easily inferred from catchment outflow concentrations alone. The sampling of all water compartments during the flood (not only stream water) and the simultaneous use of other environmental tracers, especially isotopes, appear two interesting lines for future research, in order to advance in the identification of spatial and temporal sources of catchment runoff.

Acknowledgments

This research was conducted with the support of the RespHiMed (CGL2010-18374) and EcoHyMed (CGL2013-43418) funded by the Spanish Government. The Vallcebre research catchments also operate with support from the RESEL network through an agreement between the CSIC and the Ministry of Environment. M. Roig-Planasdemunt was beneficiary of a pre-doctoral FPI grant (BES-2011-045862) and Jérôme Latron was beneficiary of a 'Ramon y Cajal' contract, both funded by the Spanish Ministry of Economy and Competitiveness. Support provided by F. Gallart, P. García-Estríngana, X. Huguet and N. Pérez-Gallego of the Surface Hydrology and Erosion Group (IDAEA-CSIC) is gratefully acknowledged.

REFERENCES

Acuña, V., *et al.* 2004. Flow extremes and benthic organic matter shape the metabolism of a headwater Mediterranean stream. *Freshwater Biology,* 49(7), 960-971.

Alvarez-Cobelas, M., *et al.* 2012. A worldwide view of organic carbon export from catchments. *Biogeochemistry,* 107(1-3), 275-293.

Aubert, A. H., *et al.* 2013. Solute transport dynamics in small, shallow groundwater-dominated agricultural catchments: insights from a high-frequency, multisolute 10 yr-long monitoring study. *Hydrology and Earth System Sciences,* 17 (4), 1379-1391.

Baron, J., Mcknight, D. and Denning, A. S. 1991. Sources of dissolved and particulate organic material in Loch Vale Watershed, Rocky Mountain National Park, Colorado, USA. *Biogeochemistry,* 15(2), 89-110.

Bernal, S., Butturini, A. and Francesc, S. 2002. Variability of DOC and nitrate responses to storms in a small Mediterranean forested catchment. *Hydrology and Earth System Sciences,* 6(6), 1031-1041.

Bernal, S., Butturini, A. and Sabater, F. 2005. Seasonal variations of dissolved nitrogen and DOC:DON ratios in an intermittent Mediterranean stream. *Biogeochemistry* 351-372.

Bishop, K., Seibert, J., Köhler, S. and Laudon, H. (2004). Resolving the double paradox of rapidly mobilized old water with highly variable responses in runoff chemistry. *Hydrological Processes*, 18(1), 185-189.

Boyer, E. W., *et al.* 1997. Response characteristics of DOC flushing in an alpine catchment. *Hydrological Processes,* 11(12), 1635-1647.

Buckingham, S., Tipping, E. and Hamilton-Taylor, J. 2008. Concentrations and fluxes of dissolved organic carbon in UK topsoils. *Science of the Total Environment,* 407(1), 460-470.

Butturini, A., *et al.* 2008. Diversity and temporal sequences of forms of DOC and NO3-discharge responses in an intermittent stream: Predictable or random succession? *Journal of Geophysical Research,* 113, G03016.

Butturini, A., *et al.* 2006. Cross-site comparison of variability of DOC and Nitrate c-q hysteresis during the autumn–winter period in three Mediterranean headwater streams: a synthetic approach. *Biogeochemistry,* 77(3), 327-349.

Butturini, A. and Sabater, F. 2000. Seasonal variability of dissolved organic carbon in a Mediterranean stream. *Biogeochemistry,* 51(3), 303-321.

Camino-Serrano, M., *et al.* 2014. Linking variability in soil solution dissolved organic carbon to climate, soil type, and vegetation type. *Global Biogeochemical Cycles*, 2013GB004726.

Carey, S. K. 2003. Dissolved organic carbon fluxes in a discontinuous permafrost subarctic alpine catchment. *Permafrost and Periglacial Processes,* 14(2), 161-171.

Carey, S. K. and Quinton, W. L. 2005. Evaluating runoff generation during summer using hydrometric, stable isotope and hydrochemical methods in a discontinuous permafrost alpine catchment. *Hydrological Processes,* 19(1), 95-114.

Christ, M. J. and David, M. B. 1996. Temperature and moisture effects on the production of dissolved organic carbon in a Spodosol. *Soil Biology and Biochemistry,* 28(9), 1191-1199.

Dawson, J. J. C., *et al.* 2008. Influence of hydrology and seasonality on DOC exports from three contrasting upland catchments. *Biogeochemistry,* 90(1), 93-113.

Dawson, J. J. C., *et al.* 2011. Seasonal controls on DOC dynamics in nested upland catchments in NE Scotland. *Hydrological Processes,* 25(10), 1647-1658.

Evansa, C. D., *et al.* 1996. Use of factor analysis to investigate processes controlling the chemical composition of four streams in the Adirondack Mountains, New York. *Journal of Hydrology,* 185(1–4), 297-316.

Gallart, F., *et al.* 2010. Hydrology in a Mediterranean mountain environment – the Vallcebre research basins (northeastern Spain). IV. Implementing and testing hydrological models. *IAHS Publ,* 336, 286-291.

Gallart, F., *et al.* 2002. Hydrological processes and their seasonal controls in a small Mediterranean mountain catchment in the Pyrenees. *Hydrology and Earth System Sciences Discussions,* 6, 527-537.

Hewlett, J. and Hibbert, A. 1967. Factors affecting the response of small watersheds to precipitation in humid areas. *Forest Hydrology,* Pergamon, 275-290.

Hinton, M. J., Schiff, S. L. and English, M. C. 1997. The significance of storms for the concentration and export of dissolved organic carbon from two Precambrian Shield catchments. *Biogeochemistry,* 36(1), 67-88.

Hinton, M. J., Schiff, S. L. and English, M. C. 1998. Sources and flowpaths of dissolved organic carbon during storms in two forested watersheds of the Precambrian Shield. *Biogeochemistry,* 41(2), 175-197.

Hudon, C., *et al.* 1996. Carbon and nutrient output from the Great Whale River (Hudson Bay) and a comparison with other rivers around Quebec. *Canadian Journal of Fisheries and Aquatic Sciences,* 53, 1513-1525.

Inamdar, S. P., Christopher, S. F. and Mitchell, M. J. 2004. Export mechanisms for dissolved organic carbon and nitrate during summer storm events in a glaciated forested catchment in New York, USA. *Hydrological Processes,* 18(14), 2651-2661.

Ivarsson, H. and Jansson, M. 1994. Temporal variations in the concentration and character of dissolved organic matter in a highly colored stream in the coastal zone of northern Sweden. *Archiv fur Hydrobiologie,* 132 (1), 45-55.

Kalbitz, K., *et al.* 2000. Control on the dynamics of dissolved organic matter in soils: A review. *Soil Science,* 165 (4), 277-304.

Kendall, K. A., Shanley, J. B. and J, M. J. 1999. A hydrometric and geochemical approach to test the transmissivity feedback hypothesis during snowmelt. *Journal of Hydrology,* 219(3–4), 188-205.

Ladouche, B., *et al.* 2001. Hydrograph separation using isotopic, chemical and hydrological approaches (Strengbach catchment, France). *Journal of Hydrology,* 242(3–4), 255-274.

Lambert, T., *et al.* 2013. Hydrologically driven seasonal changes in the sources and production mechanisms of dissolved organic carbon in a small lowland catchment. *Water Resources Research,* 49(9), 5792-5803.

Laudon, H., Berggren, M., Ågren, A., Buffam, I., Bishop, K., Grabs, T., ... & Köhler, S. (2011). Patterns and dynamics of dissolved organic carbon (DOC) in boreal streams: the role of processes, connectivity, and scaling. Ecosystems, 14(6), 880-893.

Latron, J. and Gallart, F. 2007. Seasonal dynamics of runoff-contributing areas in a small mediterranean research catchment (Vallcebre, Eastern Pyrenees). *Journal of Hydrology,* 335(1–2), 194-206.

Latron, J. and Gallart, F. 2008. Runoff generation processes in a small Mediterranean research catchment (Vallcebre, Eastern Pyrenees). *Journal of Hydrology,* 358(3–4), 206-220.

Latron, J., Llorens, P. and Gallart, F. 2009. The Hydrology of Mediterranean Mountain Areas. *Geography Compass,* 3(6), 2045-2064.

Latron, J., *et al.* 2010a. Hydrology in a Mediterranean mountain environment - The Vallcebre research basins (North Eastern Spain). I. 20 years of investigations of hydrological dynamics. *IAHS publ,* 336, 38-43.

Latron, J., *et al.* 2008. Spatial and temporal variability of the hydrological response in a small Mediterranean research catchment (Vallcebre, Eastern Pyrenees). *Hydrological Processes,* 22(6), 775-787.

Latron, J., *et al.* 2010b. Hydrology in a Mediterranean mountain environment-The Vallcebre research basins (North Eastern Spain). II. Rainfall runoff relationships and runoff processes. *IAHS Publ,* 336, 151-156.

Llorens, P., *et al.*, 2011. Hydrology and Biogeochemistry of Mediterranean Forests. *In:* LEVIA, D. F., CARLYLE-MOSES, D. and TANAKA, T. eds. *Forest Hydrology and Biogeochemistry.* Springer Netherlands, 301-319.

Llorens, P., *et al.* 2010. Hydrologyin a Mediterranean mountain environment-the Vallcebre research basins (northeastern Spain). III. Vegetation and water fluxes. *IAHS Publ,* 336, 186-191.

McDowell, W. and Wood, T. 1984. Podzolization: soil processes control dissolved organic carbon concentration in stream water. *Soil Science,* 137(1).

McDowell, W. H. and Likens, G. E. 1988. Origin, Composition, and Flux of Dissolved Organic Carbon in the Hubbard Brook Valley. *Ecological Monographs,* 58(3), 177-195.

McGlynn, B. L. and McDonnell, J. J. 2003. Role of discrete landscape units in controlling catchment dissolved organic carbon dynamics. *Water Resources Research,* 39(4), 1090.

Meyer, J. L. and Tate, C. M. 1983. The Effects of Watershed Disturbance on Dissolved Organic Carbon Dynamics of a Stream. *Ecology,* 64(1), 33-44.

Meyer, J. L., Wallace, J. B. and Eggert, S. L. 1998. Leaf Litter as a Source of Dissolved Organic Carbon in Streams. *Ecosystems,* 1(3), 240-249.

Michalzik, B.*, et al.* 2001. Fluxes and concentrations of dissolved organic carbon and nitrogen – a synthesis for temperate forests. *Biogeochemistry,* 52 (2), 173-205.

Morel, B.*, et al.* 2009. Sources of dissolved organic carbon during stormflow in a headwater agricultural catchment. *Hydrological Processes,* 23(20), 2888-2901.

Mulholland, P. J. and Hill, W. R. 1997. Seasonal patterns in streamwater nutrient and dissolved organic carbon concentrations: Separating catchment flow path and in-stream effects. *Water Resources Research,* 33(6), 1297-1306.

Neal, C.*, et al.* 2005. Dissolved organic carbon for upland acidic and acid sensitive catchments in mid-Wales. *Journal of Hydrology,* 304(1–4), 203-220.

Pan, Y.*, et al.* 2010. Study on dissolved organic carbon in precipitation in Northern China. *Atmospheric Environment,* 44(19), 2350-2357.

Peterson, B. J., Hobbie, J. E. and Corliss, T. L. 1986. Carbon Flow in a Tundra Stream Ecosystem. *Canadian Journal of Fisheries and Aquatic Sciences,* 43(6), 1259-1270.

Poyatos, R., Latron, J. and Llorens, P. 2003. Land use and land cover change after agricultural abandonment. *Mountain research and development*, 362-368.

Rubinson, K., A and Rubinson, J., F, 2000. *Análisis Instrumental.* Madrid: Prentice Hall.

Rubio, C. M., Llorens, P. and Gallart, F. 2008. Uncertainty and efficiency of pedotransfer functions for estimating water retention characteristics of soils. *European Journal of Soil Science,* 59(2), 339-347.

Schiff, S. L.*, et al.* 1997. Export of DOC from forested catchments on the Precambrian Shield of Central Ontario: Clues from 13C and 14C. *Biogeochemistry,* 36(1), 43-65.

Singh, S., Inamdar, S., Mitchell, M., & McHale, P. (2014). Seasonal pattern of dissolved organic matter (DOM) in watershed sources: influence of hydrologic flow paths and autumn leaf fall. *Biogeochemistry*, *118*(1-3), 321-337.

Soulsby, C. 1995. Contrasts in storm event hydrochemistry in an acidic afforested catchment in upland Wales. *Journal of Hydrology,* 170(1–4), 159-179.

Stutter, M. I., Dunn, S. M. and Lumsdon, D. G. 2012. Dissolved organic carbon dynamics in a UK podzolic moorland catchment: linking storm hydrochemistry, flow path analysis and sorption experiments. *Biogeosciences,* 9(6), 2159-2175.

Vázquez, E.*, et al.* 2007. Effects of the Dry–Wet Hydrological Shift on Dissolved Organic Carbon Dynamics and Fate Across Stream–Riparian Interface in a Mediterranean Catchment. *Ecosystems,* 10(2), 239-251.

Verstraeten, A.*, et al.* 2014. Impact of air-borne or canopy-derived dissolved organic carbon (DOC) on forest soil solution DOC in Flanders, Belgium. *Atmospheric Environment,* 83 (0), 155-165.

Von Schiller, D.*, et al.* 2008. Influence of land use on stream ecosystem function in a Mediterranean catchment. *Freshwater Biology,* 53(12), 2600-2612.

von Schiller, D., Graeber, D., Ribot, M., Timoner, X., Acuña, V., Martí, E., ... & Tockner, K. (2015). Hydrological transitions drive dissolved organic matter quantity and composition in a temporary Mediterranean stream. Biogeochemistry, 123(3), 429-446.

Wu, Y., Clarke, N. and Mulder, J. 2010. Dissolved Organic Carbon Concentrations in Throughfall and Soil Waters at Level II Monitoring Plots in Norway: Short- and Long-Term Variations. *Water, Air, and Soil Pollution,* 205(1-4), 273-288.

Table 1 Mean DOC concentration (mg l^{-1}, ± standard error) measured in rainwater, soil water, groundwater and stream water over the whole study period and during the dormant, vegetative, dry and wetting-up periods (n is the number of samples analysed).

	Rainwater	Soil water		Groundwater		Stream water		
		L_{cv01}	L_{cv02}	Z_{cv08}	Z_{cv35}	Baseflow	Stormflow	Total
Total	1.1±0.1	6.5±0.3	16.7±1.4	2.9±0.2	5.6±0.4	2.1±0.0	3.5±0.1	2.7±0.0
	n=187	n=60	n=32	n=70	n=32	n=349	n=228	n=577
Dormant	0.8±0.1	4.9±0.3	9.4±1.5	2.5±0.4	5±0.5	1.9±0.1	4.4±0.2	2.7±0.1
	n=42	n=19	n=10	n=19	n=13	n=79	n=39	n=118
Vegetative	1.3±0.1	7.2±0.5	20.5±1.7	3.7±0.3	5.9±0.6	2.1±0.1	3.4±0.1	2.8±0.1
	n=96	n=28	n=17	n=30	n=17	n=126	n=149	n=275
Dry	–	6.5	–	1.9±0.3	–	1.4±0.0	–	1.4±0.0
	n=0	n=1	n=0	n=3	n=0	n=13	n=0	n=13
Wetting-up	1±0.1	7.6±0.8	18.8±2.9	2.4±0.3	6.8±0.5	2.3±0.0	3.1±0.1	2.5±0.1
	n=49	n=12	n=5	n=18	n=2	n=131	n=40	n=171

Table 2 Characteristics of the rainfall-runoff events sampled during the study period.

Event date	Period	P (mm)	Q_b ($l\ s^{-1}\ km^{-2}$)	Q_p ($l\ s^{-1}\ km^{-2}$)	C_s (%)	$WT_{pre\text{-}event}$ (mm)	WT_{max} (mm)	$SWC_{pre\text{-}event}$ ($cm^3\ cm^{-3}$)	SWC_{max} ($cm^3\ cm^{-3}$)	$DOC_{pre\text{-}event}$ ($mg\ l^{-1}$)	DOC_{max} (mgl^{-1})	$Slope_{DOC/Q}$ 1[st] peak	$Slope_{DOC/Q}$ 2[nd] peak	$Slope_{DOC/Q}$ 3[rd] peak
14/05/2011	V	64.8	17.5	1728.5	41.8	-1599	0	0.39	0.40	1.7	6.8	0.005		
05/11/2011[a]	W	98.4	3.5	256.3	16.6	-3370	-666	0.38	0.43	2.4	4.4	0.019	0.010	
15/11/2011	W	61.2	7.3	183.4	21.5	-1988	-439	0.39	0.41	2.0	4.5	0.018		
22/03/2012	Do	73.4	0.1	74.0	14.9	-2932	-911	0.34	0.41	1.2	5.6	0.051		
30/04/2012	V	75.2	4.5	174.8	27.3	-1926	-364	0.39	0.41	1.8	7.2	0.050	0.020	
29/05/2012	V	34.8	15.8	2417.2	53.5	-1958	0	0.44	0.43	1.9	7.7	0.001		
19/01/2013	Do	39.6	0.1	46.5	7.5	-2482	-1587	0.34	0.38	1.5	4.7	0.058		
06/03/2013[a]	Do	68.8	0.9	279.4	33.5	-2415	0	0.35	0.41	1.5	6.4	0.037	0.014	
29/04/2013	V	109.4	4.1	321.7	33.3	-2056	0	0.36	0.39	1.8	4.9	0.040	0.010	
18/05/2013[a]	V	85.8	9.3	258.4	33.1	-1863	-283	0.38	0.43	2.1	4.8	0.030	0.012	0.009
23/07/2013	V	76.6	3.8	1918.0	18.6	-2636	-546	0.39	0.42	2.1	9.5	0.012		

Period: V=vegetative, W=wetting-up, Do=dormant; P=rainfall; Q_b=discharge at the start of the flood; Q_p=peak flow discharge; C_s=storm runoff coefficient; $WT_{pre\text{-}event}$=depth to water table (in piezometer Z_{CV08}) at the start of the flood; WT_{max}=highest level of the water table (in piezometer Z_{CV08}) during the flood; $SWC_{pre\text{-}event}$=soil water content at the start of the flood; SWC_{max}=maximum soil water content during the flood; $DOC_{pre\text{-}event}$=stream water DOC concentration at the start of the flood; DOC_{max}=maximum stream water DOC concentration during the flood; $Slope_{DOC/Q}$=slope of the linear relationship between stream water DOC concentration and discharge during a flood for the 1[st], 2[nd] and 3[rd] peak.

Figure captions

Fig. 1 Map of the Can Vila catchment, showing locations of the main instruments and of the sampling sites.

Fig. 2 Temporal dynamic of DOC concentration in rainwater during the study period (May 2011 to July 2013). White dots correspond to the concentrations of 5mm rainfall increment samples. Black dots correspond to the mean concentration of a rainfall event. The solid line is a running average. The colour scale on the x axis represents the dormant period, vegetative period, dry period and wetting-up period (see text)..

Fig. 3 Temporal dynamic (May 2011 to July 2013) of (a) soil temperature, (b) soil water content and DOC concentration in soil water (L_{CV01}), (c) depth to water table and DOC concentration in groundwater (Z_{CV08}) and (d) daily mean discharge at the outlet and DOC concentration in stream water. White dots correspond to samples DOC concentrations and black solid lines to running averages (3 values). Numbers refer to floods sampled (see Table 2). The colour scale on the x axis represents the dormant period, vegetative period, dry period and wetting-up period (see text).

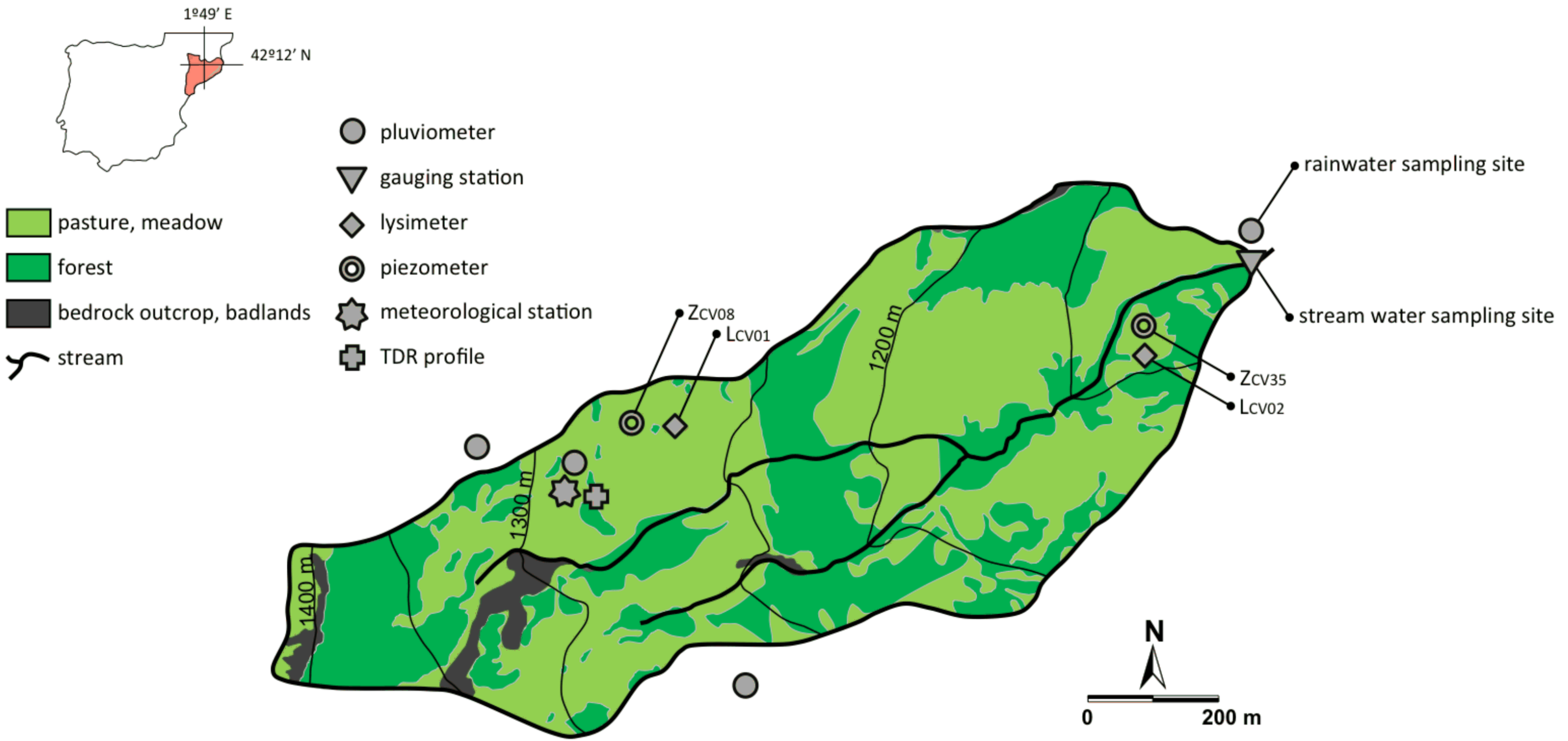
Fig. 4 Relationship between discharge measured at the outlet of the catchment and the DOC concentration in stream water. Two different dynamics are observable below and above a threshold of 20 l s^{-1} km^{-2}, roughly defining flood conditions.

Fig. 5 (a) Relationship between DOC concentration in groundwater (Z_{CV08}) and stream water. (b) Relationship between mean daily values of depth to water table (Z_{CV08}) and discharge measured at the outlet of the catchment. White dots correspond to days when groundwater and stream were sampled for DOC.

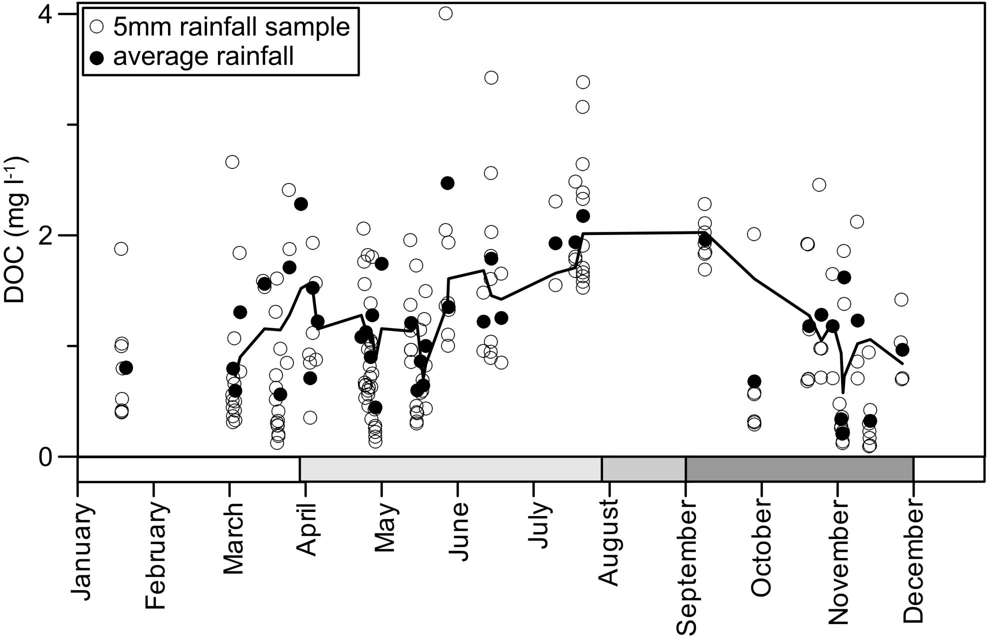
Fig. 6 (a) Discharge and DOC concentration in stream water during the 2 flood peaks of the 30/04/2012 event. (b) Relationship between discharge and DOC concentration in stream water throughout the event. (b) is the slope of the linear regressionbetween discharge and DOC concentration.

Fig. 7 Relationship between discharge and DOC concentration in stream water during dormant, vegetative and wetting-up periods. All data for the first and second peaks of floods observed during each of the periods were adjusted. (b is the slope of the linear regressionbetween discharge and DOC concentration).

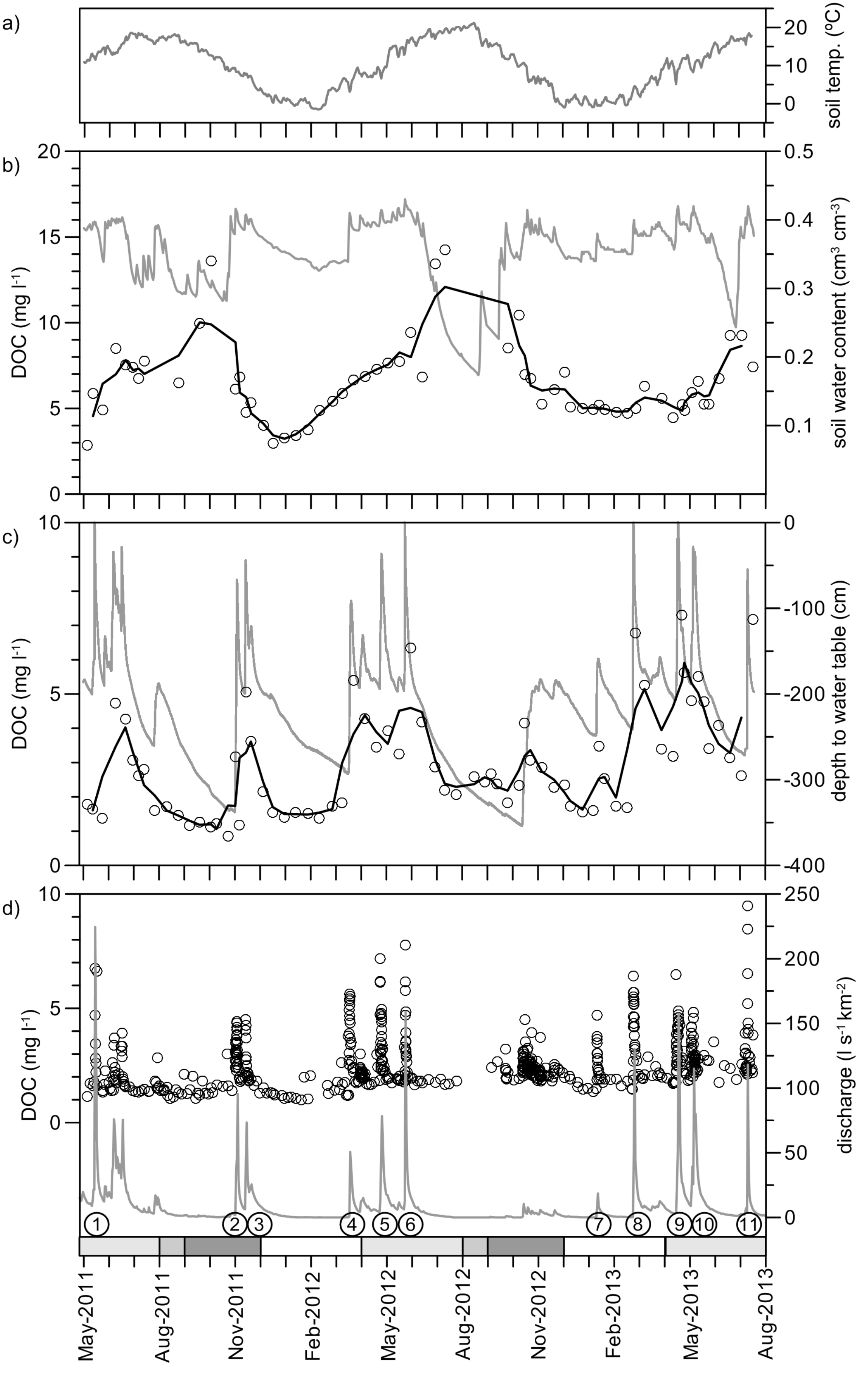
Fig. 8 (a) Discharge and DOC concentration in stream water during 3 floods observed during dormant, vegetative and wetting-up periods. (b) Relationship between discharge and DOC concentration in stream water during the event. (c) Soil water content (SWC at 0-90cm depth) and depth to the water table (piezometers Z_{CV08} and Z_{CV35}) during the event. (d) Relationship between the depth to the water table at Z_{CV08} and DOC concentration in stream water during the event. (e) Relationship between the soil water content (0-90cm) and DOC concentration in stream water during the event. In (b), (d) and (e), arrows indicate the directions of the hysteresis for each flood peak.



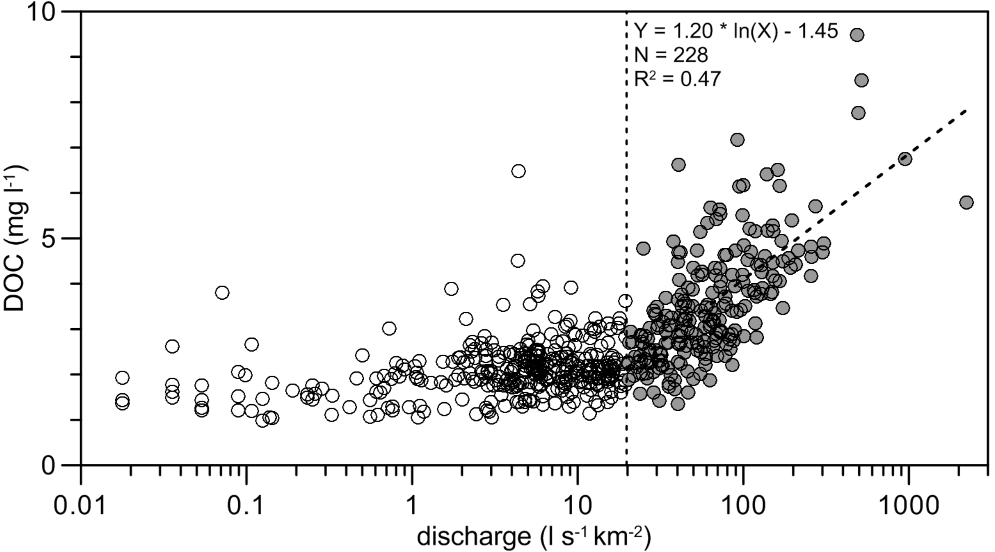
1º49′ E
42º12′ N
pasture, meadow
forest
bedrock outcrop, badlands
stream
pluviometer
gauging station
lysimeter
piezometer
meteorological station
TDR profile
rainwater sampling site
stream water sampling site
ZCV08
LCV01
ZCV35
LCV02
1200 m
1300 m
1400 m
N
0
200 m



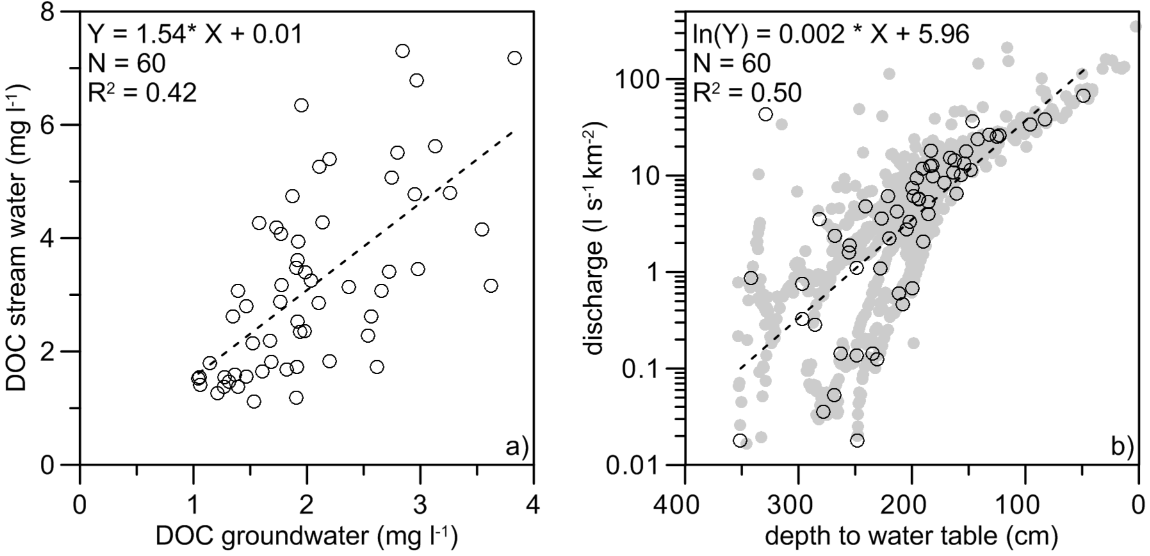
5mm rainfall sample
average rainfall
DOC (mg l-1)
0
2
4
January
February
March
April
May
June
July
August
September
October
November
December



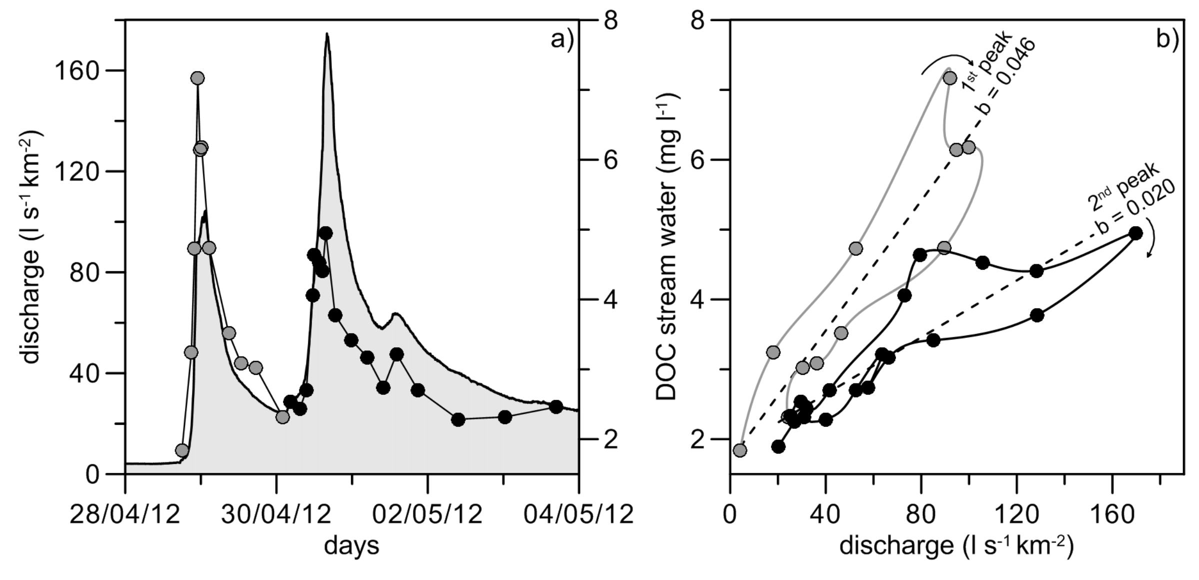
a)
b)
c)
d)
soil temp. (ºC)
DOC (mg l-1)
soil water content (cm3 cm-3)
depth to water table (cm)
discharge (l s-1km-2)
1
2
3
4
5
6
7
8
9
10
11
May-2011
Aug-2011
Nov-2011
Feb-2012
May-2012
Aug-2012
Nov-2012
Feb-2013
May-2013
Aug-2013



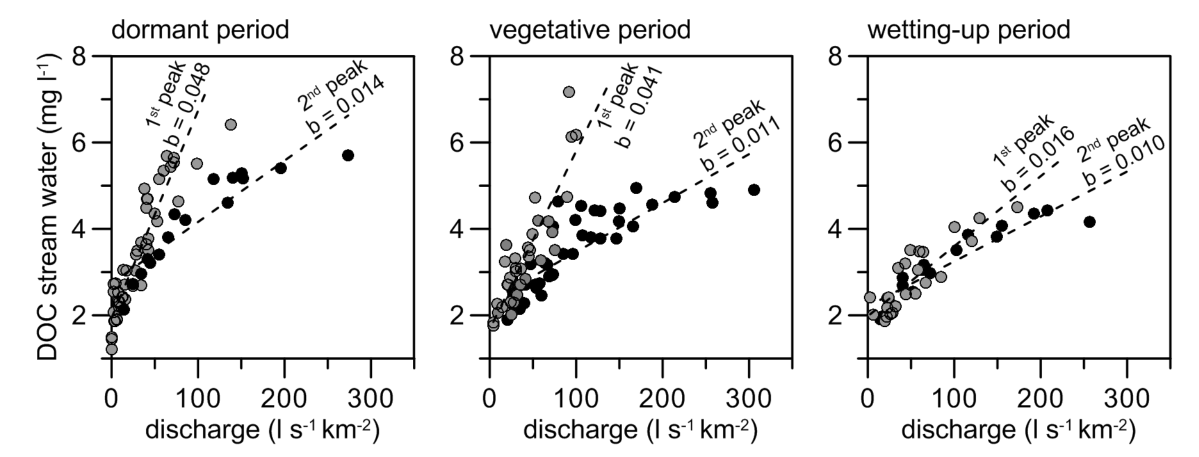
Y = 1.20 * ln(X) - 1.45
N = 228
R2 = 0.47
DOC (mg l-1)
discharge (l s-1 km-2)
10
5
0
0.01
0.1
1
10
100
1000



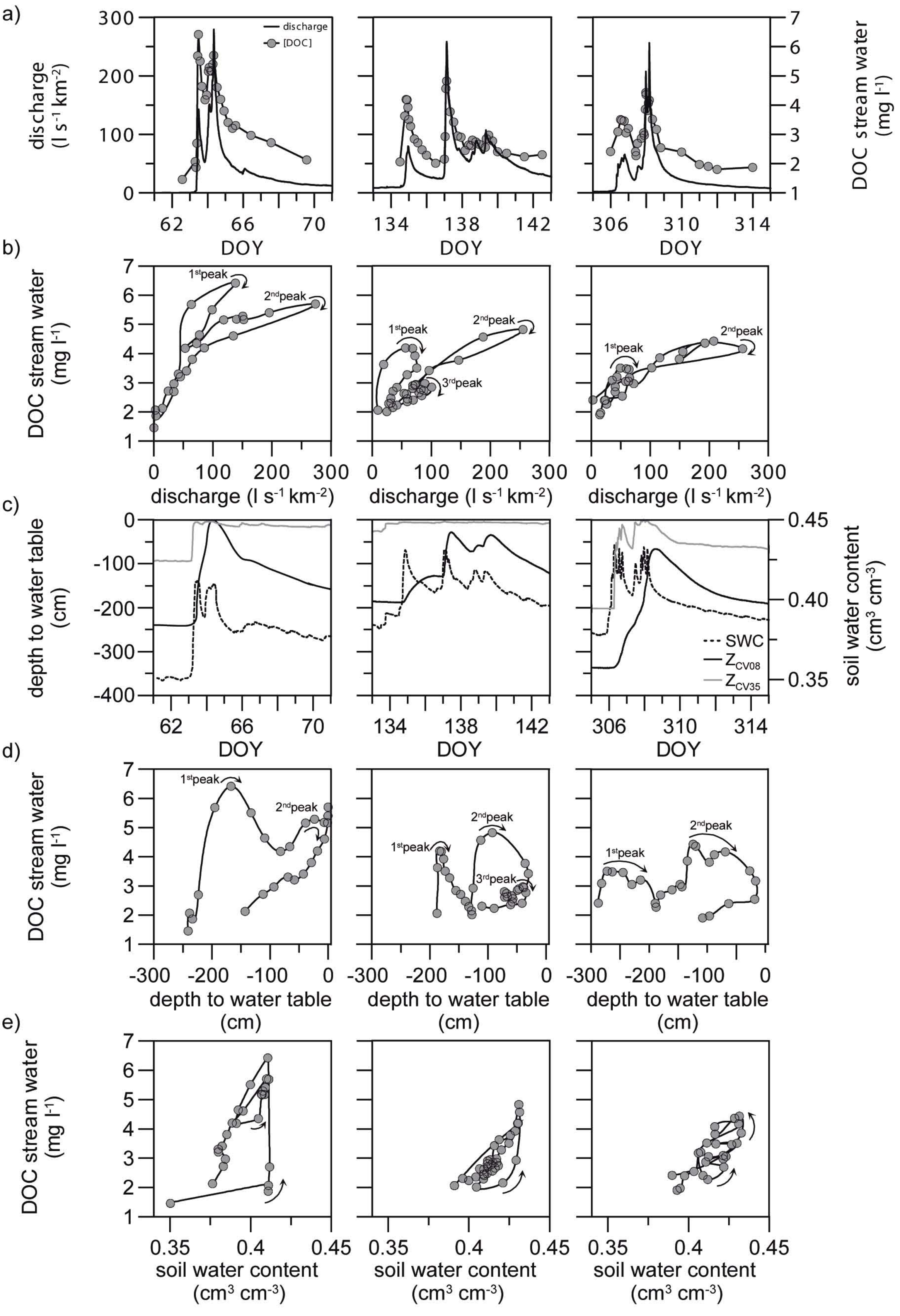
Y = 1.54* X + 0.01
N = 60
R^2 = 0.42
a)
DOC stream water (mg l-1)
DOC groundwater (mg l-1)
0
2
4
6
8
0
1
2
3
4
ln(Y) = 0.002 * X + 5.96
N = 60
R^2 = 0.50
b)
discharge (l s-1 km-2)
depth to water table (cm)
0.01
0.1
1
10
100
400
300
200
100
0



a)
discharge (l s-1 km-2)
0
40
80
120
160
2
4
6
8
28/04/12
30/04/12
02/05/12
04/05/12
days
b)
DOC stream water (mg l-1)
1st peak
b = 0.046
2nd peak
b = 0.020
0
40
80
120
160
discharge (l s-1 km-2)



dormant period
vegetative period
wetting-up period
DOC stream water (mg l-1)
discharge (l s-1 km-2)
1st peak b = 0.048
2nd peak b = 0.014
1st peak b = 0.041
2nd peak b = 0.011
1st peak b = 0.016
2nd peak b = 0.010



a)
discharge
[DOC]
discharge (l s-1 km-2)
DOC stream water (mg l-1)
DOY
b)
1stpeak
2ndpeak
3rdpeak
DOC stream water (mg l-1)
discharge (l s-1 km-2)
c)
depth to water table (cm)
soil water content (cm3 cm-3)
SWC
ZCV08
ZCV35
DOY
d)
1stpeak
2ndpeak
3rdpeak
DOC stream water (mg l-1)
depth to water table (cm)
e)
DOC stream water (mg l-1)
soil water content (cm3 cm-3)